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OCRD D/A ltr dtd 14 Jul 1972

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ELECTROLESS DEPOSITION OF NICKEL AND COBALT BASED ALLOYS

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AUG 9 1968

Introduction

The electroless deposition of nickel and cobalt from
hypophosphite-based solutions has found numerous applications by
virtue of characteristics unmatched by electrodeposition. For example,
since deposition is produced by contact of the catalytic surface
with the solution, exceptionally good deposit uniformity may be
obtained. Also, the presence of phosphorus (from hypophosphite) in
the deposits provides exceptional hardness (1) and corrosion resis-
tance (2) to nickel and valuable magnetic properties (3) to
cobalt. Electroless deposits may, in addition, be directly applied
to non-conductive materials (4). Electroless deposition of copper
(5) and palladium (6) has also been successfully applied utilizing
formaldehyde and hydrazine reducing agents respectively. In spite
of intensive investigations in this area, the electroless deposition
process, at present, is limited to the four metals mentioned above.
It was felt that electroless deposits with a wider variety of chemi-
cal, physical, and magnetic properties might be achieved by means
of codeposition of other metals during electroless nickel or cobalt
deposition. Although hydrazine, borohydride, or amine borane may
be utilized/as reducing agents for electroless nickel or cobalt
deposition, this investigation is limited to the more commonly used
hypophosphite solutions.

Nickel-tungsten and nickel-molybdenum electrodeposits (7)
are well known even though neither tungsten nor molybdenum can be
electrodeposited alone from aqueous solutions. Although the
mechanism is not clear, the electrolytic reduction of nickel ions
apparently induces reduction of tungsten and molybdenum salt to
the metal. Cobalt behaves similarly to nickel in this regard. It
was reasoned that the catalytic chemical reduction (electroless
deposition) of nickel or cobalt might induce simultaneous reduction
of tungsten and molybdenum as well as other metals.

Electroless Nickel Alloys

Experimental

Additions of sodium tungstate or molybdate were made to Brenner's acid-citrate electroless nickel solution (8):

Nickel sulfate .6H_2O - 35 g/l
Sodium citrate .2H_2O - 8.4 g/l
Sodium hypophosphite .H_2O - 10 g/l

The effects of citrate concentration and solution pH on deposit composition were determined. Electroless deposits were produced by immersing activated* platinum (50 cm^2) in 500 ml of the test solution at 98 ± 1°C for one hour. Deposit composition was determined by wet chemical analytical procedures.

The feasibility of producing other electroless nickel alloy deposits by induced chemical reduction was investigated by adding selected metal salts to each of three types of electroless nickel solutions: acid citrate, acid-acetate and ammoniated alkaline-citrate. Deposits were produced on activated (4) glass microscope slides and analyzed spectrographically for presence of elements codeposited with electroless nickel. Solutions indicated as promising for deposition of electroless nickel alloys were used for deposition on activated platinum as described above. The deposits were then analyzed for composition.

The efficiency of utilization of hypophosphite was determined during several electroless nickel and alloy deposition tests. Hypophosphite concentrations were determined using the McCloskey (9) method.

Alloy deposits on steel (as-deposited or after heat treatment at 400°C for one hour) were cross-sectioned and tested for diamond pyramidal hardness.

Selected alloy deposits were produced on activated glass microscope slides and were flaked off for determination of melting point. The alloy deposits were heated in a furnace until molten and then gradually cooled with the melting point determined by the isothermal interval during solidification.

Alloy deposits were applied to activated platinum and tested for resistance to 60 per cent (volume) hydrochloric acid or concentrated nitric acid.

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* Two minutes in 5 g/l $SnCl_2$-10 ml/l HCl; rinse;
  Two minutes in 0.2 g/l $PdCl_2$-1 ml/l HCl; rinse.

Alloy deposits of eight micron thickness were applied to steel panels and exposed to five per cent neutral salt spray for determination of corrosion resistance and protection.

Results and Discussion

The addition of sodium tungstate to the acid-citrate electroless nickel solution in the usual pH range of four to six resulted in little more than trace amounts of tungsten in deposits. However, when the pH was raised above seven (with reduced nickel content to prevent precipitation of hydroxides) substantial tungsten was produced in resultant deposits.

The effects of citrate concentration in the following evolved solution were determined in regard to electroless deposition rate and deposit composition:

Nickel sulfate .6H_2O - 7 g/l
Sodium tungstate .2H_2O - 35 g/l
Sodium hypophosphite .H_2O - 10 g/l

The solutions were adjusted to a pH of 8.2 at room temperature prior to use. The results are shown in Figure 1. The tungsten content of deposits reached a maximum level of about 20 per cent by weight with 40 g/l sodium citrate dihydrate present in the solution. The deposition rate steadily decreased with increasing citrate concentration.

The effect of solution pH on electroless nickel-tungsten deposit composition is shown in Table I. It is evident from the deposit compositions that the tungsten is present in elemental form and not as occluded oxides since the entire deposit is accounted for by the determined quantities of nickel, phosphorus and tungsten. The phosphorus content of deposits is lowest and tungsten content highest at solution pH 8.2.

The composition of deposits from the solutions at pH 8.2 containing 20 or 40 g/l sodium citrate dihydrate were determined at 68, 78 and 88 as well as 98°C. The solution temperature had little effect on deposit composition although, of course, the deposition rate decreased with decreasing temperature.

The addition of molybdate to the acid citrate electroless nickel solution prevented formation of any electroless deposits apparently by poisoning of the catalytic surface.

The results of spectrographic analysis of deposits produced from electroless nickel solution to which metal salts were added are shown in Table II. Codeposition of palladium, rhenium, tungsten, zinc or tin with electroless nickel is indicated from the ammoniated alkaline-citrate solution.

The alloy composition of deposits produced from the ammoniated alkaline-citrate solution with various metal salt additives are shown in Figure 2. Increasing zinc sulfate concentration of solution resulted in decreasing deposition rates but increasing zinc content of deposits. It is surprising that as much as 15 per cent zinc was produced in deposits considering the high electronegativity of zinc. On the other hand, tin which is much more noble than zinc and readily forms alloy electrodeposits with nickel, was not codeposited in substantial quantities with electroless nickel when sodium stannate was added to the solution. However, it has not yet been established that zinc or tin is present in deposits in the elemental form.

Increasing ratio of tungsten to nickel ion in the ammoniated alkaline-citrate solution resulted in deposits of increasing tungsten content to a maximum of approximately 12 per cent. Increasing perrhenate concentration in the electroless nickel solution resulted in increasing rhenium content of deposits to a maximum of 46 per cent at a concentration of potassium perrhenate corresponding to 1.54 g/l. It is also noteworthy that the deposit contained only two per cent phosphorus compared to about five per cent phosphorus in the electroless nickel deposit.

Rhenium is preferentially deposited to nickel in that deposits contain a larger proportion of rhenium than is present in the solution. Yet attempts to produce electroless rhenium deposits without presence of nickel ions were fruitless.

Electroless nickel-rhenium deposits were also produced containing the additional element of tungsten, zinc, or tin by addition of the appropriate metal salt to the solution that deposits a nickel - 46 per cent rhenium alloy. The following are examples of such alloys:

> 55.5% Ni - 32.7% Re - 5.1% P - 6.6% Zn
> 53.0% Ni - 44.1% Re - 1.4% P - 1.1% Sn
> 55.7% Ni - 31.5% Re - 2.6% P - 10.1% W

Electroless palladium deposition. Additions of palladium chloride to the ammoniated alkaline-citrate electroless nickel solution caused the bath to decompose after short use at the high temperature (98°C) of operation. Palladium nuclei are produced throughout the solution which provide a large surface area for rapid catalytic decomposition of the hypophosphite. This led to attempts to effect stabilization of an electroless palladium solution which might be useful in pursuing the development of electroless palladium alloys with nickel or other metals. The following solution, capable of electroless palladium deposition with good solution stability at temperatures up to 70°C was developed:

$PdCl_2$	2 g/1
NH_4OH	160 ml/1
NH_4Cl	26.8 g/1
$NaH_2PO_2 \cdot H_2O$	10 g/1

The solution was used in one case, for depositing palladium on a small specimen. This was done over a six day period at 40°C after which time a deposit approximately 175 microns thick resulted. The Vickers hardness number of the deposit was about 165 kg/mm². Addition of 30 g/1 nickel sulfate hexahydrate was made to the above electroless palladium solution and the deposit analyzed for nickel content. Palladium was preferentially deposited and only 6.0 per cent nickel was produced in the deposit along with 2.6 per cent phosphorus. Palladium alloys may be useful as diffusion barrier layers and as coatings for electronic components. The possibility of producing other electroless palladium alloys is currently under investigation.

Spectrophotometric studies. The mechanism of induced co-deposition of metal with nickel is not known. It was considered that the alloy may be produced by discharge of a complex ion containing both elements of the alloy. Attention was directed to the electroless nickel-rhenium plating solution from which deposits containing 46 per cent rhenium were obtained. Visible and ultra-violet spectrophotometric analyses were made of the solution with and without perrhenate present in order to ascertain presence of nickel-rhenium complexes. No evidence of such complexes was found from spectrophotometric studies.

Hypophosphite utilization. It was considered of interest to determine the efficiency of utilization of hypophosphite during deposition of the nickel-rhenium alloy compared to electroless nickel alone. A search of the literature revealed that about 30 to 40 per cent of the hypophosphite consumed is utilized for reduction of nickel from acid electroless nickel plating solutions with the deposit assumed to be solely nickel (10). No references were found for hypophosphite utilization from alkaline electroless nickel solutions. Perhaps one reason for others not considering phosphorus reduction in calculations is that the phosphorus reduction mechanism has not yet been established. However, it has been shown that phosphorus in deposits may originate from both hypophosphite and phosphite (11) and thus may involve a one or three electron change. For the sake of calculations of hypophosphite utilization in this report a two electron change is assumed.

An acid-citrate electroless nickel solution was tested for hypophosphite utilization and found to be 42.1 per cent efficient. (See Table III.) When no account is taken of phosphorus content but the entire deposit assumed to be nickel, the efficiency of hypophosphite utilization is 39.3 per cent which is in the range of reported values. Hypophosphite utilization tests were made with

three alkaline electroless nickel and three electroless nickel-
rhenium plating solutions. The results are shown in Table III.
The alkaline electroless nickel solution averaged about 46.6 per
cent efficiency of hypophosphite utilization or about 4.5 per cent
higher than the acid solution. The higher deposition efficiency from
the alkaline solution is probably due to decreased hydrogen ion
concentration available to compete with nickel for reduction. How-
ever, there may also be a factor of chemical dissolution of nickel
from acid solutions with an apparent decrease in reduction efficiency.
The nickel-rhenium plating solution operated at even higher efficiency,
averaging about 55.7 per cent. It is thus indicated that the nickel-
rhenium alloy is more readily deposited than electroless nickel alone.
The presently most acceptable theory of electroless deposition
mechanism is the hydride theory (12) which predicts that deposition
efficiency cannot exceed 50 per cent. For this reason, the experi-
mental evidence of deposition at greater than 50 per cent efficiency
has theoretical significance and may indicate a need for modification
of the present theory.

Properties of Deposits

Electroless nickel deposits containing zinc, tin, tungsten
or rhenium were in general not as hard as conventional nickel de-
posits from the ammoniated alkaline-citrate solution either in the
as-plated or heat treated condition.

The melting point of electroless nickel deposits from the
ammoniated alkaline-citrate solution was found to be 885°C. A
nickel-tungsten deposit of about 13 per cent tungsten had a melting
point of about 1400°C and a nickel-rhenium alloy of 46 per cent
rhenium of about 1700°C. Thus, there may be high temperature appli-
cations for the alloy deposits.

Electroless nickel - 20% tungsten deposits were quite
resistant to concentrated nitric acid being virtually unattacked
after 24 hours' immersion. Ordinary electroless nickel deposits
are rapidly attacked by concentrated nitric acid. Although electro-
less nickel is only slowly attacked by 60 per cent (volume) hydro-
chloric acid, the tungsten alloy was even more resistant to attack.
Electroless nickel-zinc deposits were on the other hand rapidly
attacked by 60 per cent hydrochloric acid.

Eight micron deposits on steel of electroless nickel
deposits containing 11 per cent zinc, two per cent tin, 13 per cent
tungsten or 46 per cent rhenium were exposed to five per cent neutral
salt spray. Deposits with zinc provided little corrosion protection.
The other alloy deposits were comparable to electroless nickel in
protective value with the rhenium alloy somewhat superior and the
tungsten alloy somewhat inferior. However, the tungsten alloy
deposit was somewhat more resistant to tarnishing than electroless
nickel. A duplex deposit of electroless nickel followed by

electroless nickel - 20% tungsten alloy appears promising for providing both corrosion protection and tarnish resistance.

Electroless Cobalt Alloys

Experimental

Additions of tungstate, perrhenate, stannate, zinc or nickel ions were made to Brenner's (8) ammoniated alkaline-citrate electroless cobalt solution:

Cobalt chloride .6H_2O	- 30 g/1
Sodium citrate .2H_2O	- 80 g/1
Ammonium chloride	- 50 g/1
Sodium hypophosphite .H_2O	- 20 g/1
Ammonium hydroxide (29%)	- 60 ml/1

Electroless deposits were produced by immersing activated platinum (50 cm^2) in 500 ml of test solution at 95 ± 1°C for one hour. Wet chemical analytical procedures were used for determination of deposit composition.

The principle application of electroless cobalt is for memory storage devices by virtue of the magnetic properties of the deposits. Thus electroless cobalt alloys were examined for coercivity and remanence compared to conventional electroless cobalt deposits using a Sperry-Rand B-H Loop Tester with drive field of 60 cycles/sec and field intensity of 1500 oersteds (13). The electroless deposits for magnetic property determinations were produced upon chemically polished copper strips (1.1 cm x 10.2 cm x 0.08 cm) activated by 30 second immersion in 0.1 g/1 $PdCl_2$ - 0.1 ml/1 HCl at 25°C.

Results and Discussion

The addition of zinc sulfate or sodium stannate to the electroless cobalt solution failed to produce significant zinc or tin in resultant electroless deposits. The effect of tungstate, perrhenate or nickel ion additions to electroless cobalt solution on the composition of deposits are shown in Figures 3, 4 and 5. The first two are examples of induced codeposition while nickel is presumably codeposited by independent ability for electroless deposition. Electroless cobalt alloy deposits were produced containing as much as nine per cent tungsten. As much as 30 per cent rhenium was produced in deposits by addition of only 0.8 g/1 potassium perrhenate to the electroless cobalt solution. Higher perrhenate concentrations caused the deposition rate to decrease to very low values. The phosphorus content and deposition rates generally decreased with increasing tungsten or rhenium content of deposits. Increasing concentrations of nickel sulfate to the electroless cobalt solution resulted in increasing deposition rates and increasing phosphorus content of deposits.

It was found that the addition of trace quantities of certain organic compounds affected the composition of electroless cobalt deposits. For example, 0.9 mg/1 phenylthiourea added to the electroless cobalt solution resulted in a decreased phosphorus content of deposits from 4.6 to 3.3. Some sulfur may also be incorporated into deposits but analysis was not made for this element.

Properties of Electroless Cobalt Alloys

Additions of one to ten g/1 sodium tungstate dihydrate to electroless cobalt solution resulted in deposits with coercivity only moderately increased over electroless cobalt alone. The remanence of deposits was not affected.

Additions of 0.3 g/1 potassium perrhenate to electroless cobalt solution provided deposits of moderately decreased coercivity but of considerably reduced remanence.

Marked increase in coercivity and remanence was provided by electroless cobalt deposits from solution containing 1 to 3 g/1 nickel sulfate hexahydrate. However, when 10 g/1 nickel sulfate was added, the coercivity of deposits became very low while remanence was retained. Such deposits may be useful for switching mechanisms since reversal of polarity may be effected with little energy consumption.

The hysteresis loops of some of the electroless cobalt alloys discussed were examined. These are shown in Figure 6 for deposits in the thickness range of 11,000 to 13,000 Å. The hysteresis loop was little affected by the deposition of cobalt-tungsten alloy. The hysteresis loop for deposits from solution containing 0.3 g/1 potassium perrhenate reflects the considerably decreased remanence. Addition of 3 g/1 nickel sulfate hexahydrate provided deposits of increased squareness as well as increased coercivity and remanence. The addition of 10 g/1 nickel sulfate provided deposits of very low coercivity but considerable remanence. Addition of 0.9 mg/1 phenylthiourea to solution produced an electroless cobalt deposit of the hysteresis loop shape shown in Figure 6 reflecting increased remanence and decreased coercivity. Thus electroless cobalt alloys may be produced to provide a variety of magnetic properties.

Little attention has been given to the corrosion protective properties of electroless cobalt. Recent studies by the authors indicate that electroless cobalt deposits provide potentially valuable protective properties to steel particularly when preceded by an electroless nickel deposit. However, electroless cobalt deposits tarnish readily when exposed to saline conditions to form a most unpleasant-appearing mottled brown condition. It was found that electroless cobalt deposits from solution containing ten g/1 sodium tungstate dihydrate or 0.9 mg/1 phenylthiourea were notably improved in resistance to tarnishing.

Conclusions

The autocatalytic chemical reduction (electroless deposition) of nickel or cobalt from alkaline solutions induces simultaneous reduction of other metal ions such as tungsten, rhenium, tin, or zinc.

Electroless nickel-tungsten alloy deposits containing up to 20 per cent tungsten are more resistant than electroless nickel to acid attack and more resistant to tarnishing during salt fog exposure. Electroless deposits of nickel-rhenium alloy contain as much as 46 per cent rhenium. The rhenium alloys are much higher in melting point than conventional electroless nickel making them potentially useful for high temperature applications. In spite of the high electronegativity of zinc, electroless nickel deposits containing as much as 15 per cent zinc are produced. Tin is also codeposited during electroless nickel deposition but only to the extent of about two per cent.

An electroless palladium-nickel alloy containing six per cent nickel is produced by addition of nickel sulfate to a newly developed electroless palladium solution.

Electroless cobalt solutions to which were added tungstate, perrhenate, nickel salt or phenylthiourea provided deposits with a wide variety of magnetic properties.

The efficiency of hypophosphite reducing agent increases during electroless deposition in the following order: acid electroless nickel, alkaline electroless nickel, alkaline electroless nickel-rhenium.

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Acknowledgement

Table I. Effect of Solution pH on Composition of Electroless Nickel-Tungsten Alloy Deposits

Solution pH	Deposit Composition, per cent by weight					
	(20 g/l sodium citrate.$2H_2O$)			(40 g/l sodium citrate.$2H_2O$)		
	Nickel	Tungsten	Phosphorus	Nickel	Tungsten	Phosphorus
5.5	-	-	-	87.50	2.88	9.48
7.0	87.50	6.68	4.80	74.64	16.58	8.62
8.2	83.75	12.68	4.38	73.50	20.48	6.53
9.5	-	-	-	72.00	18.19	9.80

Table II. Spectrographic Analysis of Deposits from Electroless Nickel Solutions to Which Various Metal Salts Were Added

Metal Salt Added	Concentration	Results of Spectrographic Tests		
		Acid-citrate	Acid-acetate	Ammoniated Alkaline-citrate
$AuCl_3.3H_2O$	0.2 g/l	(unstable solution)	(unstable solution)	(no deposit)
$PdCl_2$	"	(unstable solution)	(unstable solution)	*
$H_2PtCl_6.6H_2O$	"	(no deposit)	(no deposit)	Trace
$RhCl_3.3H_2O$	"	None	None	None
$KReO_4$	"	Trace	Trace	*
$CuSO_4.5H_2O$	0.005 moles/l	(no deposit)	(no deposit)	(no deposit)
$Na_2MoO_4.2H_2O$	"	(no deposit)	(no deposit)	(no deposit)
$Na_2WO_4.2H_2O$	"	(no deposit)	(no deposit)	*
$ZnSO_4.7H_2O$	"	(no deposit)	(no deposit)	*
$Na_2SnO_3.3H_2O$	"	-	-	*

* Detection of substantial quantities of metal codeposited with electroless nickel.

Table III. Efficiency of Utilization of Hypophosphite

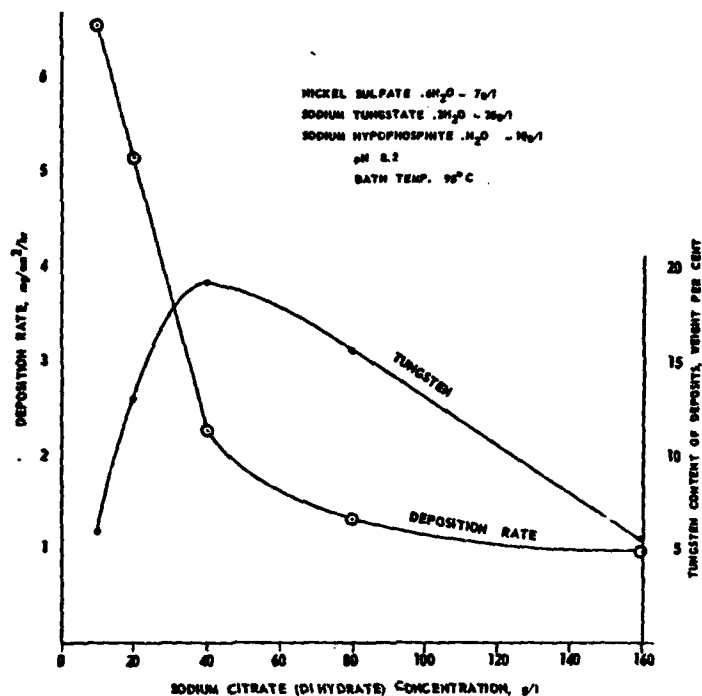| Solution Type	Deposit Composition			Per Cent Utilization of Hypophosphite
	Nickel	Phosphorus	Rhenium	
Acid-citrate	92.58	7.88	-	42.1
Alkaline-citrate	95.72	5.26	- -	47.3
"	95.48	4.94	-	44.5
"	96.20	4.62		48.5
"	55.71	2.23	43.77	51.7
"	56.21	2.26	45.73	58.8
"	52.61	1.71	46.17	56.6

FIGURE 1. Effect of citrate concentration on electroless
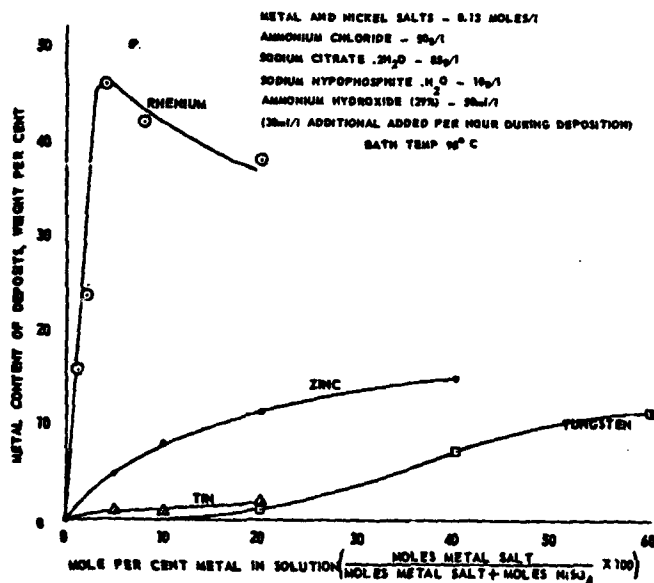deposition of nickel-tungsten alloys.

FIGURE 2. Effect of additions of perrhenate, tungstate,
stannate or zinc ions to ammoniated alkaline-citrate electroless
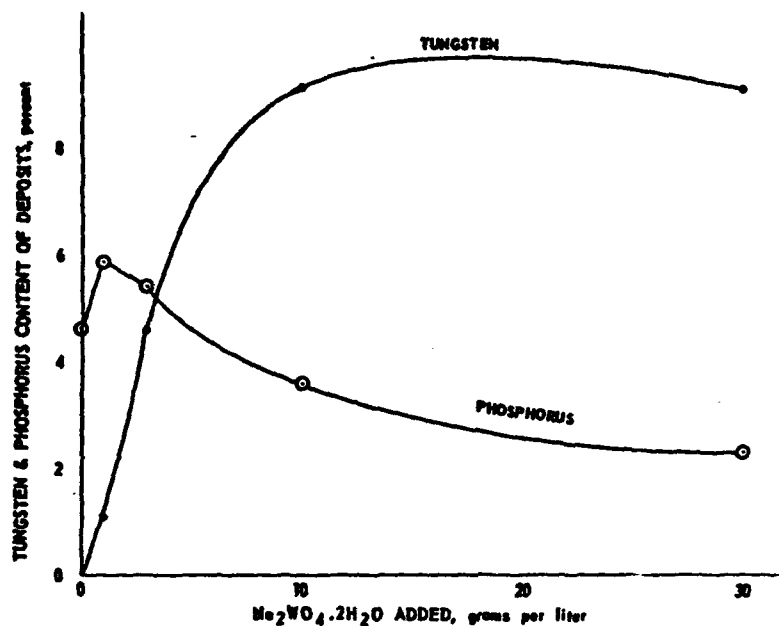nickel solution on composition of deposits.

FIGURE 3. Effect of sodium tungstate additions to electroless cobalt solution on the composition of deposits.

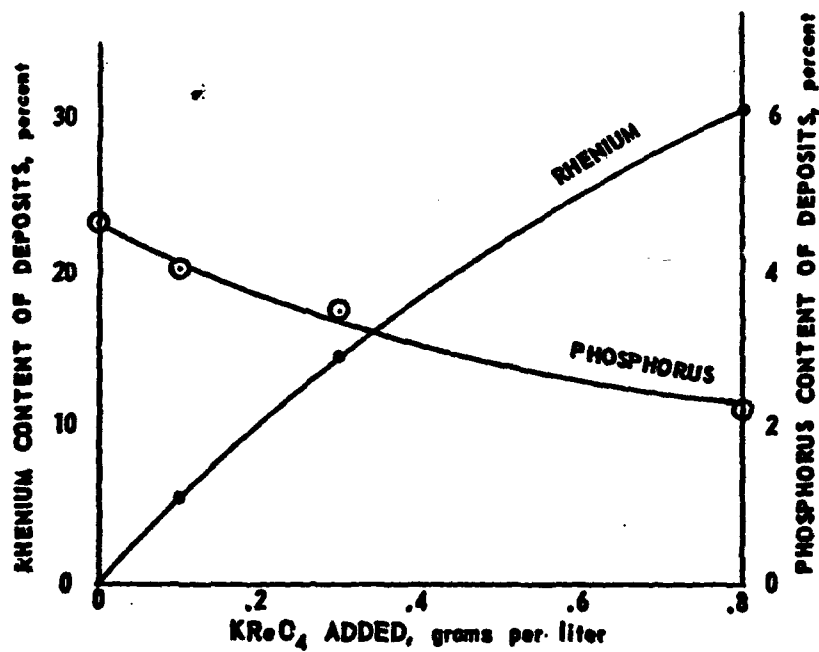**FIGURE 4.** Effect of potassium perrhenate additions to electroless cobalt solution on the composition of deposits.
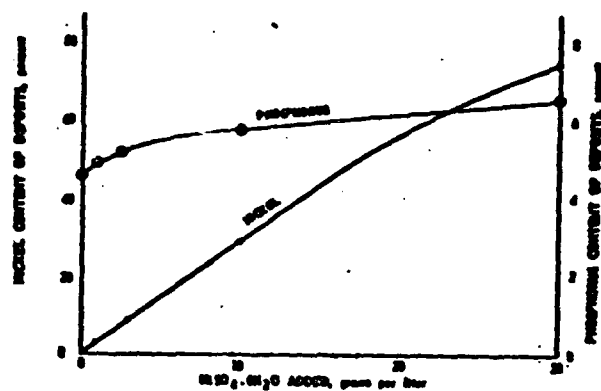
FIGURE 5. Effect of nickel sulfate additions to electroless cobalt solution on the composition of deposits.
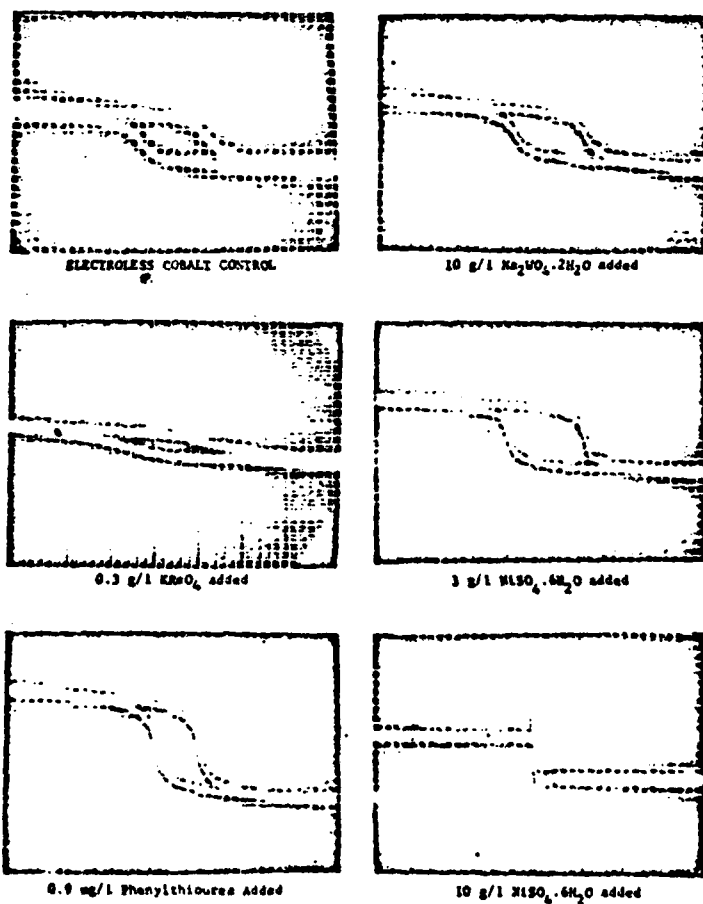

FIGURE 6. Effect of metal salt additions to electroless cobalt solution on the hysteresis loops of deposits (11,000 to 13,000 Å thick).